# PARENTAGE OF THE LOCAL EXCITED ELECTRONIC STATE OF ETHENE COORDINATED IN ZEISE'S SALT*

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The excited Rydberg state (without spin label) of the free ethene molecule with the electronic configuration $(np\pi_x)^1 (2p\pi_x)^1$ (where $2p\pi_x$ means the $\pi$ orbital) was deduced as a geometric model of the coordinated ethene. In the neighbourhood of Pt, the geometry of $C_2H_4$ ligand corresponds to one of the two mirror conformations of the free excited $C_2H_4$ in a double-minimum potential well related to the in-phase $CH_2$ wagging vibration ($\nu'_{12}$ after Mulliken or $\nu'_7$ after Herzberg). The population of $np\pi_x$ Rydberg orbitals of the ethene results in a small lengthening of the CC bond (about 1%). The local excited state of the ligand is assumed to be realized due to forward- and back-donation bonds of $\sigma$ symmetry and not those of $\pi$ symmetry. Conversion of $C_2H_4$ to a non-rigid ligand with large-amplitude, out-of-plane $CH_2$ motions is the main consequence of the Pt–ethene coordination bond. A new interpretation of the temperature dependence of lines in the $^1$H-NMR spectrum of Zeise's salt is suggested.

Recently[1], a new model of the ethene–PtCl$_3$ coordination bond in Zeise's salt (further ZS), K[(C$_2$H$_4$)PtCl$_3$].H$_2$O, has been outlined. The use of the widely accepted concept of the electron forward- and back-donations between the alkene and the transition metal species leads to local excited states of both $C_2H_4$ and PtCl$_3$ moieties composing the electronic ground state of Zeise's anion, [(C$_2$H$_4$)PtCl$_3$]$^{(-)}$. The local electronic state of the coordinated ethene is comparable, as to its vibrational frequencies and geometry, to an electronic excited (Rydberg) state of the free ethene molecule and not to either singlet or triplet $(\pi^*)^1 (\pi)^1 \ldots$ states[1]. The similarity between the coordinated ethene and the free $C_2H_4^+$ in its ionic ground state has been pointed out[2,3] and was based mainly on anomalous isotopic shifts in the CC stretching frequency ($\nu'_2$) which for the coordinated $C_2D_4$ and free $C_2D_4^+$ is higher than that for the coordinated $C_2H_4$ and free $C_2H_4^+$, respectively. So, Zeise's anion seems to be the favorable case where the effective lowering of electron density in the original $\pi$ orbital of ethene due to $\sigma$ forward-donation to Pt is comparable to the removal of one electron from the same orbital in the free $C_2H_4$ (a near-radical cation model[1]). However, the full agreement between the properties of the free ion and of the ligand has not been found: they differ in the CC bond lengths and geometries (141 pm *vs* 135 to 137 pm and point symmetry $D_2$ *vs* $C_{2v}$). The Rydberg states of the free ethene molecule or of the free negative ion $C_2H_4^{(-)}$ offer better models for the coordinated $C_2H_4$. The reason is that the Rydberg electron(s) is(are) located far outside the ion core and so the free molecule (or the negative ion) and its positive ion core are expected to have similar vibrational spacings[4,5]. Moreover, these Rydberg states, presumably of different geometries, offer a larger variety of possibilities

whereas the radical cation represents only an extreme model for the coordinated $C_2H_4$. A justification of this approach can be found in the MO study[6] of the $Ag^+$–ethene complex. Hosoya and Nagakura[6] have included the $3s$ Rydberg orbital of $C_2H_4$ into the calculation and proved (by semi-empirical SCF–LCI) the importance of the Rydberg transition in the alkenic part of the complex. To a certain extent a back-donation bond of $\sigma$ symmetry represents such Rydberg transition in the ligand.

The aim of this work is to find a Rydberg state of free $C_2H_4$ which, according to its geometry and vibrational frequencies, could serve as a model of the local excited state of the coordinated ethene.

## RESULTS

### The Rydberg States of Free $C_2H_4$ (the parent state)

The Rydberg states of the free molecule have been extensively studied. A recent non-empirical study[7] is the most complete, since $s$, $p$, and $d$ functions have been included in the Gaussian basis set (cf. also[8,9]). The virtual Rydberg MO's of ethene are summarized in Table I in the order of increasing energy of the vertical transition (singlet $Ry \leftarrow \pi$). Symmetries of the Rydberg orbitals and molecular states are related to the $D_{2h}$ point group to which planar $C_2H_4$ in the ground state belongs. The orientation of the Cartesian axes $(x, y, z)$ is that according to Mulliken, i.e., the z-axis is colinear with the C=C bond and all the nuclei lie in the $(y, z)$ plane. In the semi-UAO approximation, there are nine Rydberg orbitals belonging to seven different symmetry types.

The intention is to decide which of the nine Rydberg states of the free $C_2H_4$ molecule can serve as a geometric model of the ethene coordinated in Zeise's anion. As to the $C_2H_4$ ligand in crystalline ZS, the four experimental facts can be stated: 1) The coordinated $C_2H_4$ is not planar (local point symmetry $C_{2v}$, cf. Fig. 1a and ref.[10]); 2) the CC bond length is not too much elongated after the coordination (133·9 pm for free[11], 135·4 pm for the ligand[10]; about 1%); 3) all CH bonds of the ligand have the same length[10]; 4) the midpoint of the CC distance is 20 pm above the $PtCl_3$ plane and the CC bond is not perpendicular to it (84·2°, ref.[12]).

Starting from the fact that the $C_2H_4$ ligand is non-planar, one can omit all Rydberg orbitals located in the original $(y, z)$ plane, namely $p_y(np\pi_y)$, $p_z(np\sigma)$, and $d_{yz}(nd\pi_y)$. Moreover, for some of the corresponding Rydberg states of free $C_2H_4$ there are experimental data which justify this omission (Table I). Several Rydberg series have been found in the high resolution UV absorption spectrum of gaseous ethene[13]. For instance, the CC bond length of 141 pm has been calculated for the singlet $3s$ Rydberg state and the $D_2$ point symmetry has been deduced[14,15]. On the basis of both data it is possible to exclude the $3sR$ state ($B_3$ for $D_2$) as the model of the coordinated $C_2H_4$. Also all the $nsR$ states for $n > 3$ can be excluded, since the

$D_2$ symmetry is presumably preserved throughout the series including the limiting $C_2H_4^+$. In another case, the Rydberg orbitals $nd\pi_x$ ($n \geqq 4$) derived from $nd_{xz}$ AO's are the analogues of the $\pi^*$ antibonding orbital in the valence shell. Population of this orbital in free $C_2H_4$ leads to excited states, again with $D_2$ or $D_{2d}$ symmetry[14,16]. For this reason its Rydberg analogues are excluded, too. The Rydberg MO's formed from the $nd_{z^2}$, $nd_{x^2-y^2}$, and $nd_{xy}$ ($n \geqq 3$) carbon AO's can be ruled out on the basis of the calculated CC bond lengths[7] (Table I).

By this elimination procedure the $np_x$ carbon AO's remain which form the $np\pi_x$ Rydberg MO's (for both $n \geqq 3$). These orbitals are analogous to the $\pi$ bonding orbital in the valence shell of the free ethene molecule in the ground state. Presumably, one of the corresponding Rydberg transitions has been detected in the treshold electron energy loss spectrum of free ethene[17]. However, in any case the geometric data for this Rydberg state are still lacking.

TABLE I

Classification[a] of the Lowest Rydberg Singlet States of Free Ethene According to their Symmetry and Geometrical Properties (from[7])[b]

| AO[c] | RyMO[d] | OS[e] | SS[f] | Acceptability | Because of[g] |
|---|---|---|---|---|---|
| $(\pi)$ | $(2p\pi_x)$ | $(1^{st}b_{3u})$ | $(^1A_g)$ | — | — |
| $(\pi^*)$ | $(3d\pi_x)$ | $(1^{st}b_{2g})$ | $(^{1,3}B_{1u})$ | no | $144-180$[h], $D_{2d}$ or $D_2$ |
| $3s$ | $3s$ | $4^{th}a_g$ | $^1B_{3u}$ | no | $141$, $D_2$ |
| $3p_y$ | $3p\pi_y$ | $2^{nd}b_{2u}$ | $^1B_{1g}$ | no | antibonding CH[i] |
| $3p_z$ | $3p\sigma$ | $3^{rd}b_{1u}$ | $^1B_{2g}$ | no | $144$, $D_2$ |
| $3p_x$ | $3p\pi_x$ | $2^{nd}b_{3u}$ | $^1A_g$ | yes? | see text |
| $3d_{z^2}$ | $4d\sigma$ | $5^{th}a_g$ | $^1B_{3u}$ | no | $139$ |
| $3d_{x^2-y^2}$ | $3d\delta'$ | $6^{th}a_g$ | $^1B_{3u}$ | no | $141$ |
| $3d_{xy}$ | $3d\delta''$ | $1^{st}b_{1g}$ | $^1B_{2u}$ | no | $141$ |
| $3d_{yz}$ | $4d\pi_y$ | $2^{nd}b_{3g}$ | $^1A_u$ | no | antibonding CH[i] |
| $3d_{xz}$ | $4d\pi_x$ | $2^{nd}b_{2g}$ | $^1B_{1u}$ | no | analog of $\pi^*$ |

[a] Acceptability of the Rydberg state as the "parent" of the local excited electronic state of co-ordinated $C_2H_4$. [b] The valence shell orbitals $\pi$(HOMO) and $\pi^*$(LUMO) are also included for comparison. [c] Atomic orbital of carbon atom. [d] Virtual Rydberg MO's in the semi-UAO approximation; the number is the principal quantum number. [e] Symmetry of the Rydberg orbital (in $D_{2h}$ group) and its ordering number in ethene molecule. [f] Symmetry of the Rydberg singlet state in $D_{2h}$ point group. [g] Exluded as the parent because of CC bond length $r_{cc}$ (in pm $= = 10^{-12}$ m) or point symmetry or antibonding character (from ref.[7]). [h] From ref.[16]. [i] Population of the Rydberg orbital would lead to a significant lenghtening of CH bonds or to their nonequivalence which is not the case[10] of ZS: 110 $vs$ 108·5 pm in free[11].

### The $np\pi_x \leftarrow \pi$ Rydberg Transitions in Free $C_2H_4$

According to the electric dipole selection rules for optical spectra, these transitions $(n \geqq 3)$ are symmetry forbidden in the planar configuration of nuclei $(A_g \leftarrow A_g$ in $D_{2h}$, cf. Table II), since the terminating Rydberg orbitals $np\pi_x$ belong to the same symmetry species $b_{3u}$ as the starting $\pi$ orbital $(2p\pi_x)$. This bonding molecular orbital $\pi$ is doubly occupied in the ground state and these two $\pi$ electrons are mainly responsible for the stability of the planar configuration of nuclei[18]. The promotion (or removal) of one of them means a considerable loosening of this rigidity[18]. In other words, the excited ethene molecule should be regarded as a non-rigid molecule, the equilibrium geometry of which can take the form of one of the three out-of-plane distorsions (Fig. 1). As a consequence of different geometries in the initial and final states, the allowedness of the transition must be determined on the basis of the lower symmetry[18], in this case of the excited state. It is clear that out-of-plane displacements of the nuclei lead to a descent in the point symmetry of $C_2H_4$ molecule. The Rydberg transitions $(np\pi_x) \leftarrow (\pi)$ become symmetry allowed in the point group $C_{2v}$ (Table II). Then, the geometry of the nuclear configuration has the form

TABLE II

Electric Dipole Selection Rules for Rydberg Transitions $Ry \leftarrow \pi$ in Ethene with Different Non-planar Geometries[a]

| Type of carbon AO $(n \geqq 3)$ | $s$ | $p_y$ | $p_z$ | $p_x$ | $d_{z^2}$ | $d_{x^2-y^2}$ | $d_{xy}$ | $d_{yz}$ | $d_{xz}$ |
|---|---|---|---|---|---|---|---|---|---|
| Rydberg MO in semi-UAO approx. | $3s$ | $3p\pi_y$ | $3p\sigma$ | $3p\pi_x$ | $4d\sigma$ | $3d\delta'$ | $3d\delta''$ | $4d\pi_y$ | $4d\pi_x$ |
| Orbital symmetry in $D_{2h}$ | $a_g$ | $b_{2u}$ | $b_{1u}$ | $b_{3u}$ | $a_g$ | $a_g$ | $b_{1g}$ | $b_{3g}$ | $b_{2g}$ |
| Symmetry of the Rydberg state | $B_{3u}$ | $B_{1g}$ | $B_{2g}$ | $A_g$ | $B_{3u}$ | $B_{3u}$ | $B_{2u}$ | $A_u$ | $B_{1u}$ |
| Electric Dipole[b] Selection Rule[c] in — $D_{2h}(B_{1u}, B_{2u}, B_{3u})$[d] | $\perp$ | f. | f. | f. | $\perp$ | $\perp$ | $\perp$ | f. | C=C |
| $D_2(B_1, B_2, B_3)$[e] | $\perp$ | C=C | f. | f. | $\perp$ | $\perp$ | $\perp$ | f. | C=C |
| $C_{2v}(A_u, B_u, B_u)$[f] | f. | f. | f. | $\perp$ | $\perp$ | $\perp$ | $\perp$ | f. | C=C |
| $C_{2v}(A_1, B_1, B_2)$[g] | $\perp$ | $\perp$ | C=C | $\perp$ | $\perp$ | $\perp$ | $\perp$ | f. | C=C |
| $C_2(A, B, B)$[h] | $\perp$ | $\perp$ | $\perp$ | $\perp$ | $\perp$ | $\perp$ | $\perp$ | $\perp$ | $\perp$ |

[a] The non-equivalence of CH bonds or of HCH angles is not considered. For symbols cf. Table I. [b] The symmetry species of the Cartesian components of electric dipole are in parentheses $(M_z, M_y, M_x)$. [c] If allowed then polarization indicated (C=C means along the CC bond, $\perp$ means in plane or along an axis perpendicular to the CC bond), otherwise forbidden (f.). [d] Planar geometry. [e] Twisted geometry, cf. Fig. 1b. [f] Axes $z$ and $y$ are interchanged; cf. Fig. 1c. [g] Axes $z$ and $x$ are interchanged, cf. Fig. 1b. [h] This geometry corresponds to a combination of the in-phase (Fig. 1a) or out-of-phase (Fig. 1c) $CH_2$ wagging with the CC torsion (Fig. 1b); cf. the geometry of hydrazine molecule $H_2NNH_2$ in the ground state[29,30].

of the in-phase $CH_2$ wagging vibration $(v_{12}(b_{3u})$ according to Mulliken or $v_7(b_{1u})$ according to Herzberg) of the originally planar $C_2H_4$ (Fig. 1a).

Let us consider a one-electron transition $(np\pi_x)^1 (\pi)^1 \ldots \leftarrow (\pi)^2 \ldots$ for $n \geq 3$ in the free ethene molecule which is vibronically allowed[19] by the excitation of an odd number of quanta of $v_{12}$. This transition would lead to the excited Rydberg state with the geometry belonging to $C_{2v}$. However, it is clear that there exist two out-of--plane conformations with $C_{2v}$ symmetry which are mirror images of themselves in the original molecular plane $(y, z)$. Such expectation should be formulated in terms of the potential curves with two equivalent minima separated by a barrier to inversion[20] of $C_2H_4^*$ (cf. Fig 1 in the preceding paper). If the height of the barrier is low, the lifetime of each conformation is short, depending on the inversion frequency of the $C_2H_4^*$ species. The time average of geometries of both $C_{2v}$ conformations then represents effectively the planar configuration of nuclei, i.e., the point group of symmetry $D_{2h}$. Consequently, the CC bond length need not increase extensively because the analogy between the $\pi$ and $np\pi_x$ orbitals always leads to the electronic configuration $(np\pi_x)^1 (2p\pi_x)^1 \ldots$ So, it seems that the expected geometric properties of free $C_2H_4$ in these excited Rydberg states agree with the geometric properties of the coordinated ethene in its local excited state in Zeise's anion. Finally, it should be pointed out that with the free $C_2H_4$ molecule the $(y, z)$ mirror plane divides the space into two half-spaces which are equivalent except the handedness, i.e., one is "clockwise", the other "counterclockwise".

*Model of the Local Excited State of the Coordinated Ethene*

The neighbouring of ethene and Pt atom in Zeise's anion stipulates a non-equivalence of the two half-spaces mentioned above. First, the $\sigma$ forward-donation of electrons from the $\pi$ orbital of ethene to Pt reduces the CC bond order and the local electronic state of the ligand can be regarded as the free $C_2H_4^+$ in its ionic ground state[2,3]. Then, the back-donation of electrons from Pt to ethene causes
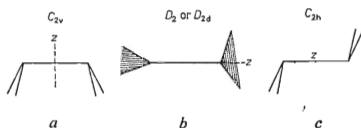


FIG. 1

Three Non-planar Geometries of $C_2H_4$ and the Corresponding Out-of-plane Normal Vibrations

*a* $v_{12}$ (Mulliken[16]) or $v_7$ (Herzberg[20]), in-phase $CH_2$ wagging; *b* $v_4$, CC torsion ($CH_2$ twisting); *c* $v_7$ (Mulliken) or $v_8$ (Herzberg), out-of-phase $CH_2$ wagging.

its local excitation which can be interpreted as a formation of the excited states (valence or Rydberg) of the free neutral molecule or of the free negative ion $C_2H_4^{(-)}$. Recently[1] the $(\pi^*)^1 (\pi)^1 \ldots$ excited states of the free $C_2H_4$ as the model for the local electronic state of the coordinated species have been excluded because of differences in the CC bond length and $C_2H_4$ geometry. In other words, a population of the $\pi^*$ antibonding orbital of ethene in Zeise's anion by back-bonding with Pt cannot be significant ($cf.$ also[2]). It does not mean that the whole back-donation mechanism is insignificant. It does mean, however, that the back-donation bond of $\pi$ symmetry is less important than the $\sigma$ back-donation which "has hitherto been overlooked"[6]. For this reason, additional unoccupied (Rydberg) orbitals of $C_2H_4$ should be taken into account. This was indicated in the preceding sections where the $np\pi_x$ Rydberg orbitals and the corresponding $A_g$ Rydberg states were selected on the basis of their estimated geometric properties.

From this point of view the local excited state of the ligand can be regarded as the excited Rydberg state of the free neutral molecule or as the doubly excited Rydberg state of the free negative ion $C_2H_4^{(-)}$. As it has been noted, these free excited species and their positive ion core are expected to have similar vibrational spacings[4,5]. So, a similar situation is expected to occur in the coordinated species. The back-donation bond does not cancel the effects of the forward-donation bond — (the non-rigidity of the positive ion-like core) — but it brings about a preferential geometry of the ligand, depending on the type of the Rydberg orbital to be populated. If the population of the $np\pi_x$ Rydberg orbital prevails, a double minimum potential curve related to the $\nu_{12}$ vibration should be taken into account. However, the "left" and "right" $C_{2v}$ conformations of $C_2H_4$ in the neighbourhood of Pt are no more equivalent. Instead, one of them is preferred as an equilibrium geometry of the ligand. In fact, this has been found in the crystalline Zeise's salt[10] ($cf.$ Fig. $1a$ and Fig. 2 in the preceding paper). As a consequence, the CC bond distance of $C_2H_4$ is not markedly elongated after the coordination, the increase amounting to 1% of the original value ($133 \cdot 9 \to 135 \cdot 9$ pm)[10].

For these reasons the local point symmetry $C_{2v}$ of the ligand is still applicable, even though the „overall" symmetry of Zeise's anion descends to $C_s$ due to an oblique CC bond orientation with respect to the $PtCl_3$ plane.

The anomalous isotopic upward shift of the CC stretching frequency $\nu_2'$ in the coordinated ethene-$d_0$ and -$d_4$ is an additional problem connected with the local excited state of the ligand. The ionic ground state of the free $C_2H_4^+$ and $C_2D_4^+$ species is assumed to be the convergence limit of all the Rydberg series in ethene[7], $e.g.$, of the $nsR$ series, too. However, for the first member, $3sR$ state, this anomaly was not observed. In contrary, the $\nu_2'$ values ($1370 \to 1295$ cm$^{-1}$) fit usual isotopic rules[13]. On going from the $3sR$ state to $C_2H_4^+$, it is possible to assume a gradual change in the usual isotopic downward shift of $\nu_2'$ to an anomalous upward one with increasing $n$. Experimental data are, however, lacking. An analogous consideration

should apply to all the Rydberg series. Even in this model, the main consequence of $C_2H_4$ coordination is the conversion of ethene molecule to a non-rigid ligand with large-amplitude, out-of-plane motions of the $CH_2$ groups.

Finally, the assumed local excited state of the $PtCl_3$ moiety is worthy of note. A local excitation of $PtCl_3$ should be manifested by a lengthening of the Pt—Cl bond(s). This has been found in the crystalline ZS for the $(Pt—Cl)_{opp}$ bond opposite to the ethene ligand[12]. The lowered $\nu(Pt—Cl)_{opp}$ frequency has been observed in the vibrational spectra, along with a lowering in $^{35}Cl$ and $^{81}Br$ frequencies in the NQR spectra of ZS and its bromo analogue[21,22]. A weakening of the $(Pt—Cl)_{opp}$ bond has been verified also by calculation[23]. These facts are usually explained by introducing the general and self-explanatory term the ,,*trans*-effect" (of $C_2H_4$ ligand in this case). It can be also explained by a local excitation of $PtCl_3$. To localize the pseudo-excitation into the $(Pt—Cl)_{opp}$ bond, a four-centre MO involving only the $C_2PtCl_{opp}$ grouping seems to be more convenient, however, a pyramidal distorsion of $PtCl_3$ is needed.

## DISCUSSION

Till this moment, only singlet Rydberg states were implicitly considered here. An instantaneous objection can arise in that these states of the free ethene molecule are situated well above of the $(\pi^*\pi)$ states and their population in the coordination bond would be negligible. However, taking into consideration the spin-orbit coupling constant of Pt metal $(4052\ cm^{-1})$[24], relatively high values can also be expected for $Pt^{2+}$ and its complex groupings like $PtCl_3$ in Zeise's anion. A strong singlet–triplet mixing could play its role in the model of ethene ligand but the problem is very complex[23,25]. Any spin labelling was omitted of the local electronic state of the ligand for that reason. Pure triplet Rydberg states of free ethene, as an extreme case, are energetically closer to the $(\pi^*\pi)$ states[16] and it makes the objection less restricting.

The MO's of Zeise's anion have been studied by SCF Xα-scattered wave method for the CC bond perpendicular to the $PtCl_3$ plane[23].

It has been found[23] that the $\pi$ back-bonding into the ethene $\pi^*$ orbital is rather less important than the $\sigma$-bonding, amounting perhaps to at most 25% of the total bonding of ethene to Pt. On the other hand, the $\pi$ orbital of ethene undergoes very significant mixing with Pt orbitals and contributes nearly equally to the $5a_1$, $6a_1$, and $7a_1$ orbitals[23]: ,,Apparently the classic argument of $\sigma$-donation from the ethylene $\pi$-orbital to the empty $d_{z^2}$ orbital of Pt is somewhat too simplistic, as this description applies only to the $5a_1$ orbital". The other two $\sigma$-orbitals involve the ethene $\pi$-orbital with a combination of the Pt $d_{z^2}$ and $d_{x^2-y^2}$ orbitals and the latter is important in describing the $\sigma$-bond between ethene and Pt.

The importance of the $d_{x^2-y^2}$ orbital of metal atom interacting with the ethene orbitals has been already pointed out by Hosoya and Nagakura[6]. It is especially

valid for cases of oblique orientations of the ethene molecule with respect to the „coordination" plane (cf.[26]) which also applies to Zeise's anion[12]. At a qualitative level, the $Pt^{2+}$ orbital $d_{z^2}$ or $d_{x^2-y^2}$ (formally, one being empty, the other occupied) participates on both $\sigma$ forward- and $\sigma$ back-bonding, in dependence on their relative population and difference in the orbital energies. However, additional empty orbitals of ethene should be taken into account.

Generally, authors disagree in their estimates of the strength of the coordination bond in Zeise's anion (cf. refs cited in[1]). Now, there are some experimental data proving indirectly a strong Pt–ethene interaction. The study of X-ray photoelectron spectrum of ZS showed that even the $1s$ electron binding energy in carbons of the ligand is lowered with respect to the free $C_2H_4$ molecule[27] ($284\cdot9 \to 283\cdot4$ eV). The change by $1\cdot5$ eV gives some experimental support to the calculations of Rösch and coworkers who have found a shift of all higher ethene levels by about $0\cdot8$ eV after coordination[23]. The lowering in orbital energies is a better measure of the strength of the Pt–ethene bonding than the lowering in vibrational frequencies of the $C_2H_4$ ligand. Both data, however, prove accordingly the strong interaction between Pt and ethene.

It follows from the above mentioned shifts that also the average excitation energy ($\Delta E_{av}$) is changed. Hence, the comparison of the chemical shifts and spin-spin interaction constants in the NMR spectra of the free and coordinated $C_2H_4$ should consider this change of $\Delta E_{av}$. Such attempt has not yet been done. Furthermore, the temperature dependence of the $^1H$-NMR spectra of ZS has been interpreted as a consequence of the more or less hindered internal rotation of $C_2H_4$ as a whole with respect to the $PtCl_3$ plane[28]. We believe that our concept of large amplitude $CH_2$ internal vibrations (CC torsion or $CH_2$ twisting and in-phase $CH_2$ wagging) in the ligand can also explain this temperature dependence. In other words, the NMR spectra of the coordinated species are the spectra of $C_2H_4$ in an electronically or vibronically excited-like state.

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*Note added in proof:* Mulliken recently changed the ordering of unoccupied MO's of ethene: LUMO is the 3s Rydberg orbital, the $\pi^*$ orbital is LUMO+2 (J. Chem. Phys. *66*, 2448 (1977)).